

THE REVERSIBLE DISSOCIATION OF
PENTAARYLETHANES

A DISSERTATION
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF SCIENCE
IN THE UNIVERSITY OF MICHIGAN

BY
FREDERICK YAGER WISELOGLE

1936

Reprinted from THE JOURNAL OF ORGANIC CHEMISTRY
Vol. 1, No. 4, September, 1936



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41551510_0108



THE RELATIVE STABILITY OF PENTAARYLETHANES. III.¹ THE REVERSIBLE DISSOCIATION OF PENTA- ARYLETHANES*

W. E. BACHMANN AND F. Y. WISELOGLE

Received October 2, 1936

It is well known that hexaarylethanes in solution undergo spontaneous, reversible dissociation into triarylmethyl radicals. Tetraarylethanes, on the other hand, are remarkably inert substances which show no indication of dissociation even at high temperatures. Pentaarylethanes occupy a somewhat intermediate position with regard to stability. At room temperature a solution of pentaphenylethane is colorless and does not absorb oxygen or decolorize iodine to any appreciable extent as triarylmethyl radicals do. If the solution is warmed to about 105°, however, the yellow color of triphenylmethyl develops, and may be removed completely by shaking the cooled solution with air or by adding a small amount of iodine. If the solution is heated to 180–200° the pentaphenylethane is rapidly decomposed and *s*-tetraphenylethane may be isolated among the decomposition products.² Solid pentaphenylethane decomposes at its melting point, which is lower in air than in nitrogen.³ At 100–120° pentaphenylethane is rapidly cleaved by bromine to give triphenylmethyl bromide and diphenylmethyl bromide and by hydrogen iodide to give triphenylmethane and diphenylmethane.¹ Even at room temperature the carbon-carbon ethane linkage is broken by potassium.⁴ These reactions indicate a weak carbon-carbon bond in pentaphenylethane with dissociation taking place at slightly elevated temperatures.

Three years ago we began a study of the influence of "dissociating" groups on the properties of pentaarylethanes, and found that the groups can be arranged in the following order of decreasing ability to weaken the ethane linkage:¹ 1-naphthyl, *p*-biphenyl, *p*-anisyl, *p*-tolyl, phenyl, bi-

¹ II, BACHMANN, *J. Am. Chem. Soc.*, **55**, 3005–3010 (1933).

* From the Sc.D. dissertation of F. Y. Wiselogle.

² SCHLENK AND HERZENSTEIN, *Ber.*, **43**, 3542 (1910).

³ BACHMANN, *J. Am. Chem. Soc.*, **55**, 2135–2139 (1933).

⁴ SCHLENK AND MARCUS, *Ber.*, **47**, 1670 (1914).

phenylene/2. We have now undertaken the synthesis of the complete homologous series of pentaarylethanes containing phenyl and *p*-biphenyl groups in order to study the effect of introducing a large number of "dissociating" groups in the pentaarylethane molecule.*

SYNTHESIS OF THE PENTAARYLETHANES

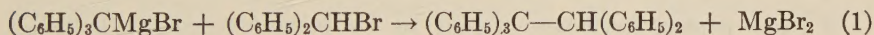
There are, in all, eleven pentaarylethanes theoretically derivable from pentaphenylethane through successive replacement of the five phenyl groups by *p*-biphenyl groups (Table I). We have prepared a number

TABLE I
PENTAARYLETHANES CONTAINING PHENYL AND *p*-BIPHENYL GROUPS

SYMBOL*	$R_5C^{1,2}CHR_2$
0-	$(C_6H_5)_3C-CH(C_6H_5)_2$
2-	$(C_6H_5)_3C-CH(C_6H_5)(C_6H_4-C_6H_5-p)$
2,2-	$(C_6H_5)_3C-CH(C_6H_4-C_6H_5-p)_2$
1-	$(p-C_6H_5-C_6H_4)(C_6H_5)_2C-CH(C_6H_5)_2$
1,2-	$(p-C_6H_5-C_6H_4)(C_6H_5)_2C-CH(C_6H_5)(C_6H_4-C_6H_5-p)$
1,2,2-	$(p-C_6H_5-C_6H_4)(C_6H_5)_2C-CH(C_6H_4-C_6H_5-p)_2$
1,1-	$(p-C_6H_5-C_6H_4)_2(C_6H_5)C-CH(C_6H_5)_2$
1,1,2-	$(p-C_6H_5-C_6H_4)_2(C_6H_5)C-CH(C_6H_5)(C_6H_4-C_6H_5-p)$
1,1,2,2-	$(p-C_6H_5-C_6H_4)_2(C_6H_5)C-CH(C_6H_4-C_6H_5-p)_2$
1,1,1-	$(p-C_6H_5-C_6H_4)_3C-CH(C_6H_5)_2$
1,1,1,2-	$(p-C_6H_5-C_6H_4)_3C-CH(C_6H_5)(C_6H_4-C_6H_5-p)$
1,1,1,2,2-	$(p-C_6H_5-C_6H_4)_3C-CH(C_6H_4-C_6H_5-p)_2$

* The symbols (0-, 1-, etc.) throughout the paper refer to the positions of the biphenyl groups on the "1" carbon atom (with three aryl groups) and the "2" carbon atom (with two aryl groups) of the pentaarylethane; thus pentaphenylethane is called 0-, penta-*p*-biphenylethane is 1,1,1,2,2-, etc.

of these by coupling the Grignard reagent of a triarylbromomethane with a diarylbromomethane³ (Equation 1).

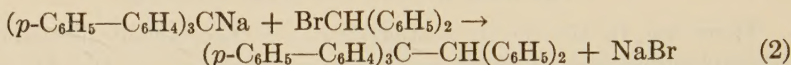


Triphenylbromomethane and diphenyl-*p*-biphenylbromomethane give highly satisfactory yields of the Grignard reagents, from which the desired pentaarylethanes may be prepared without difficulty. Phenyl-di-*p*-biphenylmethylmagnesium bromide was obtained in quantitative yield, but the coupling reaction with diphenylbromomethane was unsatisfactory. Tri-*p*-biphenylbromomethane forms an insoluble double salt with mag-

* It will be recalled that hexa-*p*-biphenylethane is completely dissociated in solution as well as in the solid state; SCHLENK, WEICKEL AND HERZENSTEIN, *Ann.*, **372**, 1-7 (1910); MÜLLER, MÜLLER-RODLOFF AND BUNGE, *Ann.*, **520**, 235 (1935).

nesium bromide which coats the remaining magnesium and prevents further reaction; moreover, prolonged refluxing results in reduction of the double salt to tri-*p*-biphenylmethane through the action of the ether.

Since the Grignard reaction was not generally applicable, the more reactive triarylmethylsodium compounds, which react instantly with diarylbromomethanes were employed (Equation 2). This method has the



further advantage over the Grignard reaction that the entire process is carried out at room temperature. By this method all the remaining pentaarylethanes were synthesized in 50–90 per cent. yields.

TABLE II
TEMPERATURE AT WHICH COLOR DEVELOPS
(SOLVENT: ETHYL BENZOATE)

PENTAARYLETHANE	TEMP., °C.	COLOR	COLOR OF R ₂ C—
0-	105	yellow	yellow
2-	92	yellow	yellow
2,2-	90	yellow	yellow
1-	88	orange-red	orange-red
1,2-	88	orange-red	orange-red
1,2,2-	80	orange-red	orange-red
1,1-	83	light red	light red
1,1,2-	83	light red	light red
1,1,2,2-	82	light red	light red
1,1,1-	81	dark red	dark red
1,1,1,2-	78	dark red	dark red
1,1,1,2,2-	71	dark red	dark red

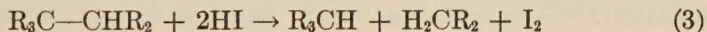
PROPERTIES OF THE PENTAARYLETHANES

All our pentaarylethanes proved to be relatively stable, colorless, crystalline compounds. They are quite soluble in chloroform and in benzene at room temperature, giving colorless solutions from which the compounds may be precipitated by addition of alcohol. They exhibit a pronounced tendency to crystallize with solvent of crystallization, which is held tenaciously, and in a few cases exhibit polymorphism, existing in two crystalline forms possessing different melting points. The melting points of the compounds are lower in air than in nitrogen, as was found to be the case with the pentaarylethanes previously prepared.³ Even in an inert atmosphere the compounds melt over a temperature range and the solids generally acquire a color several degrees below the melting point.

The dissociation of pentaphenylethane giving triphenylmethyl radicals has been indicated in the formation of a yellow color on heating a solution to 105°. The effect of the *p*-biphenyl group in promoting dissociation of pentaarylethanes was established in a semi-quantitative way by determining the temperature at which a solution of the pentaarylethane first developed a visible color. In Table II are shown the lowest temperatures at which color could be detected by looking through 10 cm. of a 0.02 molar solution of the pentaarylethanes in ethyl benzoate when the solutions were heated at the rate of 2° per minute. If dissociation occurs on warming then, *a priori*, the colors of the solutions should correspond to the colors of the free triarylmethyl radicals. It is seen that such is the case. Moreover, increasing the number of *p*-biphenyl groups in the molecule, in general, lowers the temperature at which color becomes visible. In every case the color could be discharged completely by quickly cooling the solution and shaking it with air. The appearance of color was often observed during recrystallization of the pentaarylethanes from hot solutions, and for final purification the compounds were dissolved in chloroform or benzene at room temperature and precipitated by alcohol.

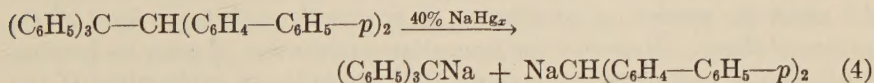
CLEAVAGE OF THE PENTAARYLETHANES BY HYDROGEN IODIDE

All the pentaarylethanes are converted quantitatively to a mixture of triarylmethane and diarylmethane by hydrogen iodide in acetic acid at 120° (Equation 3). By this reaction the structures of our pentaarylethanes were confirmed.



CLEAVAGE BY SODIUM AMALGAM

Although pentaphenylethane is not cleaved by liquid 40 per cent. sodium amalgam within twenty-four hours, all the pentaarylethanes containing two or more *p*-biphenyl groups, regardless of their positions, are quantitatively cleaved into triarylmethylsodium and diarylmethylsodium

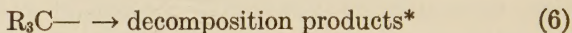
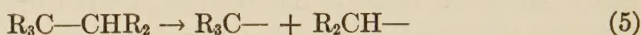


(Equation 4). Cleavage of the two pentaarylethanes containing but one *p*-biphenyl group is about one-half complete in this length of time. From these results it is evident that an increase in the number of *p*-biphenyl groups reduces the resistance of the carbon-carbon bond to scission. There was no cleavage of any of the pentaarylethanes by one per cent. sodium amalgam, a reagent known to react with triarylmethyl radicals, which proves that the reaction with the more concentrated amalgam is a direct

cleavage of the weak carbon-carbon bond and not a reaction involving radicals.

REVERSIBLE DISSOCIATION OF PENTAARYLETHANES

The dissociation of pentaarylethanes into triarylmethyl and diarylmethyl radicals is evidenced by the formation of triarylmethyl radicals in warm solutions of the hydrocarbons and by the formation of *s*-tetraarylethanes when the pentaarylethanes are decomposed by heating them in ethyl benzoate solution (Equations 5-7). Since the triarylmethyl radicals



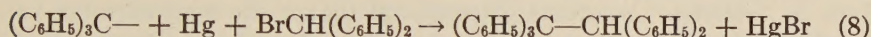
undergo complete decomposition at the boiling point of ethyl benzoate (213°) and the *s*-tetraarylethanes do not dissociate at this temperature thermal decomposition of the pentaarylethanes goes rapidly to completion under these conditions.

Since the appearance of color on heating is an indication of dissociation, then it should be possible to obtain *s*-tetraarylethanes by heating solutions of pentaarylethanes to temperatures just above those at which color appears, for the formation of the *s*-tetraarylethanes is an irreversible process. In agreement with this view, *s*-tetraphenylethane was obtained in 30 per cent. yield when a solution of pentaphenylethane in toluene was refluxed (110°) for seventeen hours. Some unchanged pentaphenylethane was recovered, however, an indication that decomposition was incomplete even after this length of time. Similarly, penta-*p*-biphenylethane gave only two per cent. of *s*-tetra-*p*-biphenylethane after being heated for two hours in *o*-dichlorobenzene at 100°, the original compound being recovered in 87 per cent. yield. This relative stability of pentaarylethanes, in marked contrast to their reactivity at these temperatures, made it seem very probable that *the dissociation of pentaarylethanes is a reversible reaction for which the position of equilibrium is practically entirely in favor of the pentaarylethane*. Moreover the immediate appearance of color on heating a solution of pentaarylethane above 100° precludes an explanation of the stability in terms of a slow irreversible dissociation process. The reversible dissociation was definitely proved from a study of the kinetics of oxidation, for it was shown that in a *colorless* solution of pentaphenylethane at 95° a rapid dissociation into triphenylmethyl and diphenylmethyl

* For the thermal decomposition of triphenylmethyl see SCHMIDLIN, "Das Triphenylmethyl," Ferdinand Enke, Stuttgart, 1913, p. 85.

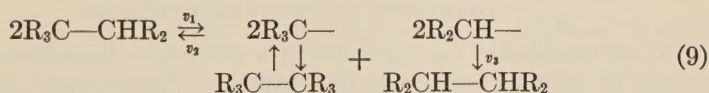
radicals is taking place; this means, of course, that the radicals are recombining to form pentaphenylethane as fast as they are formed.

With the dissociation reaction already established we have obtained proof that the reverse reaction, the union of triarylmethyl and diarylmethyl radicals, can take place. Interaction of mercury and triphenylchloromethane or triphenylbromomethane gives triphenylmethyl, which associates nearly completely to hexaphenylethane. Similarly, mercury and diphenylbromomethane give *s*-tetraphenylethane. If now mercury and diphenylbromomethane are shaken together in presence of triphenylmethyl radicals, the principal product is the unsymmetrical compound, pentaphenylethane, which we have isolated in 88 per cent. yield (Equation 8). Similarly, if an equimolecular mixture of triphenylchloromethane and



diphenylbromomethane is shaken with mercury, the sole product is pentaphenylethane, which can be isolated in nearly quantitative yield. It is apparent that the triphenylmethyl and diphenylmethyl radicals combine in preference to association of like radicals. This reaction suggests that a similar "capture" of the diphenylmethyl radical by the triphenylmethyl radical to form pentaphenylethane may take place in the original Gomberg and Cone⁵ synthesis of the hydrocarbon in which a mixture of triphenylchloromethane and diphenylbromomethane is treated with activated magnesium.

We may now formulate the equilibria existing in a pentaarylethane solution at slightly elevated temperatures (50–100°) (Equation 9). From



the results of kinetic studies to be described later it will be shown that a rapid dissociation into radicals is taking place in solutions of pentaarylethanes which do not show a visible color. This means that the primary dissociation equilibrium ($v_1 = v_2$) must be reached instantly at all temperatures and the position of equilibrium must be nearly entirely in favor of the pentaarylethane. Moreover, we know that diarylmethyl radicals cannot exist in any appreciable concentration. Now, the irreversible formation of an extremely small amount of *s*-tetraarylethane results in a corresponding increase in the concentration of triarylmethyl radicals (under these conditions hexaarylethanes are completely dissociated); as a result the *equilibrium* concentration of diarylmethyl radicals is reduced to such an extent that their association is practically stopped. The

⁵ GOMBERG AND CONE, *ibid.*, **39**, 1466 (1906).

velocity of formation of pentaarylethane from the radicals, v_2 , is a constant, independent of the concentration of diarylmethyl radicals under these conditions; the rate of formation of *s*-tetraarylethane, v_3 , however, diminishes as the square of the concentration of diarylmethyl radicals. The formation of every molecule of *s*-tetraarylethane decreases the rate of formation of the next molecule. The concentration of triarylmethyl radicals is always much greater than the concentration of diarylmethyl radicals. Visual proof is found in the fact that the color, arising from the presence of triarylmethyl radicals, in a warm pentaarylethane solution does not disappear on cooling the solution in absence of oxygen. This precludes measurement of the extent of equilibrium from the intensity of the color as is done in the case of dissociation of symmetrical compounds. Even in "colorless" solutions of pentaarylethanes the concentration of diarylmethyl radicals must be much less than that of the triarylmethyl radicals.

The rate of thermal decomposition of pentaarylethanes, at 100° or at 200°, is dependent, then, on the rate of decomposition of the excess of triarylmethyl radicals (Equation 6) and not on the rate of formation of the *s*-tetraarylethane (Equation 7); in support of this statement is the failure to accumulate any appreciable amount of triarylmethyl radicals in the thermal decomposition experiments. It should be borne in mind, however, that from a thermodynamic standpoint a pentaarylethane solution is an unstable system which in infinite time would disproportionate completely into hexaarylethane and *s*-tetraarylethane.

OXIDATION OF PENTAARYLETHANES

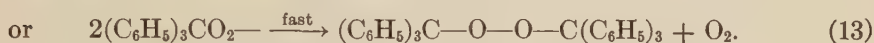
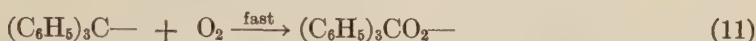
Having established the existence of a reversible dissociation process we set out to determine the rate at which this dissociation proceeds. One of the most characteristic reactions of triarylmethyl radicals is a rapid absorption of oxygen to form triarylmethyl peroxides. Because the rate of absorption of oxygen by hexaphenylethane increases somewhat, but not proportionately, with an increase in the partial pressure of oxygen Mithoff and Branch⁶ concluded that two competing reactions were involved, the one a rapid coupling of oxygen with the free triphenylmethyl radicals resulting from a relatively slow dissociation, the other a direct and also relatively slow reaction between hexaphenylethane and oxygen. By decreasing the concentration of hexaphenylethane and lowering the partial pressure of oxygen Ziegler⁷ found that the rate of absorption of oxygen followed a first-order reaction and was independent of the oxygen pressure.

⁶ MITHOFF AND BRANCH, *J. Am. Chem. Soc.*, **52**, 255-268 (1930).

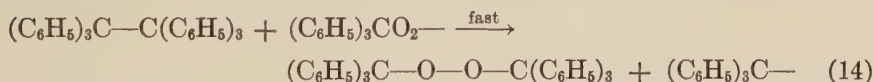
⁷ ZIEGLER, EWALD, AND ORTH, *Ann.*, **479**, 277-303 (1930).

The rate of oxidation, under these conditions, was identical with the rate of reaction between hexaphenylethane and iodine⁷ or nitric oxide,⁸ and was in no case dependent on the concentration of the added reagent. Since the same rate was obtained in these three different reactions the rate-controlling step in each is undoubtedly the velocity of dissociation of hexaphenylethane into triphenylmethyl radicals. That the oxygen absorption by triphenylmethyl solutions involves only a reaction between radicals and oxygen and no direct reaction of the oxygen with hexaphenylethane was shown from a study of the effect of oxygen inhibitors and acceptors.^{9,10}

The mechanism of oxidation is formulated as follows (Equations 10–13):



The normal triphenylmethyl peroxide, a secondary product, results from the interaction of the primary unstable addition compound of triphenylmethyl and oxygen, $(\text{C}_6\text{H}_5)_3\text{CO}_2-$, with another triphenylmethyl radical (Equation 12), or with another peroxide radical (Equation 13), or through cleavage of hexaphenylethane (Equation 14). The regenerated tri-



phenylmethyl may then pick up another molecule of oxygen and repeat the process; these chain reactions account for the increase in rate of absorption of oxygen with an increase in the oxygen pressure. Under the experimental conditions the chains are very short; therefore the addition of traces of oxidation inhibitors produces no apparent change in the rate of oxidation.

In the presence of one equivalent or more of an oxidation inhibitor, suitably pyrogallol, the total absorption of oxygen by hexaphenylethane is doubled; *i.e.*, two moles of oxygen are absorbed by one mole of hexaphenylethane; furthermore, the rate of absorption of oxygen, a first-order reaction independent of the oxygen pressure or pyrogallol concentration, is identical with the rate of dissociation as determined by the

⁸ ZIEGLER, ORTH, AND WEBER, *ibid.*, **504**, 131–161 (1933).

⁹ ZIEGLER AND EWALD, *ibid.*, **504**, 162–181 (1933).

¹⁰ ZIEGLER, EWALD, AND SEIB, *ibid.*, **504**, 182–189 (1933).

three methods just described. The loosely bound hydrogen atoms in the pyrogallol stabilize the active peroxide radicals (Equation 15) before they



can undergo any of the reactions leading to the formation of triphenylmethyl peroxide (Equations 12–14). Under these conditions each triphenylmethyl radical captures and holds one molecule of oxygen and all chain reactions are eliminated. Since the rate of reaction is identical with the rate of dissociation, a direct reaction between hexaphenylethane and oxygen is eliminated from consideration, for the rate of this second-order reaction should not be affected by the presence of the pyrogallol but would be proportional to the oxygen pressure.

The close relationship between pentaarylethanes and hexaarylethanes is clearly brought out from oxidation studies. Although solutions of our pentaarylethanes are relatively inert at room temperature we found that

TABLE III
TIMES REQUIRED FOR 0.00125 MOLAR SOLUTIONS OF PENTAARYLETHANES IN
o-DICHLOROBENZENE TO ABSORB 0.5 MOLE OF OXYGEN AT 100°*

COMP.D.	MIN.	COMP.D.	MIN.	COMP.D.	MIN.	COMP.D.	MIN.
0-	4.5	1-	3.5	1,1-	2.5	1,1,1-	2.0
2-	3.5	1,2-	2.5	1,1,2-	1.5	1,1,1,2-	1.0
2,2-	2.5	1,2,2-	1.5	1,1,2,2-	1.0	1,1,1,2,2-	0.8

* The effect of replacing phenyl groups on the "1" carbon by biphenyl groups is apparent from reading horizontally; the effect of introducing biphenyl groups on the "2" carbon is shown in the vertical columns.

they rapidly absorb oxygen when warmed.† Semi-quantitative measurements of the rate and extent of absorption were made in a steam cone at 100°. In all cases the rate of absorption of oxygen was a maximum at the beginning of the run, rapidly falling off until a more or less constant value was reached after 1.1 to 1.2 mole of oxygen per mole of pentaarylethane had been absorbed; the absorption did not completely cease even after one hour. The times required for the pentaarylethanes to absorb 0.5 mole of oxygen have been estimated from the data and are presented in Table III. In every case it will be noticed that successive replacement of phenyl groups by *p*-biphenyl groups accelerates the rate of absorption of

* WIELAND AND MAIER, *Ber.*, **64**, 1205–1210 (1931), have prepared triphenylmethyl-hydrogen peroxide, $(\text{C}_6\text{H}_5)_3\text{C—O—O—H}$, and found it to be unstable even at room temperature unless very pure.

† TSCHITSCHIBABIN, *Ber.*, **40**, 368 (1907), observed that pentaphenylethane solutions in hot nitrobenzene absorb oxygen but gave no experimental details.

oxygen; this result is in striking agreement with the reaction between these pentaarylethanes and 40 per cent. sodium amalgam.

NATURE OF THE OXIDATION PRODUCTS

The chief product of the oxidation of a pentaarylethane at 100° was found to be the unsymmetrical triarylmethyl-(diarylmethyl)-peroxide, $R_3C-O-O-CHR_2$,* in addition a small amount (5–10 per cent.) of the symmetrical bis-triarylmethyl peroxide, $R_3C-O-O-CR_3$, was usually found. For the isolation of the unsymmetrical peroxide it was found more practical to work up the reaction mixture as soon as one mole of oxygen had been absorbed; by following this procedure it was possible to isolate six crystalline peroxides in yields of 50–80 per cent. of the calculated amount. In contrast to the symmetrical triarylmethyl peroxides, these unsymmetrical peroxides are all readily soluble in the common organic solvents and crystallize from them with considerable difficulty.

The structures of the unsymmetrical peroxides were established through cleavage by 2 per cent. sodium amalgam (Equation 16); hydrolysis of the



cleavage products gave the triarylcarbinol and diarylcarbinol corresponding to the triarylmethyl and diarylmethyl radicals originally present in the pentaarylethane. In agreement with this result is the appearance of the color characteristic of the sulfates of the triaryl- and diarylcarbinols when the peroxides are dissolved in sulfuric acid.

MECHANISM OF THE OXIDATION REACTION

The formation of unsymmetrical triarylmethyl-(diarylmethyl)-peroxides as the chief product of the oxidation reaction suggested that the oxygen cleaves the carbon-carbon bond of the pentaarylethanes directly. A study of the kinetics of the reaction has shown, however, that this mechanism cannot be correct; instead the reaction proceeds only through the intermediate formation of triarylmethyl and diarylmethyl radicals. Indeed, the measurement of the rate of oxidation has yielded the rate of dissociation of the pentaarylethane.

If the oxidation reaction involves the direct oxidation of the pentaarylethane, a bimolecular reaction, then the rate, dx/dt , should be dependent not only on the concentration of the ethane, $a - x$ (a being the

* SCHMIDLIN, "Das Triphenylmethyl," Ferdinand Enke, Stuttgart, 1913, p. 145, allowed a solution of pentaphenylethane to stand four weeks at room temperature in an oxygen atmosphere, removed the benzene and dissolved the oil in sulfuric acid; hydrolysis gave a trace of triphenylcarbinol and he concluded that the intermediate product was the unsymmetrical peroxide.

initial concentration of pentaarylethane, and x the amount reacted in time t), but also on the oxygen pressure, p_{O_2} :

$$dx/dt = k(a - x)p_{O_2}.$$

If, on the other hand, the reaction proceeds only through radicals, which are so rapidly oxidized that the rate of oxidation depends on the velocity of dissociation, then the speed of the reaction would be independent of the oxygen concentration, for the dissociation process is a unimolecular reaction,

$$dx/dt = k(a - x).$$

Under the conditions of the absorption experiments the reaction, whether unimolecular or bimolecular, would be of the first order since the partial

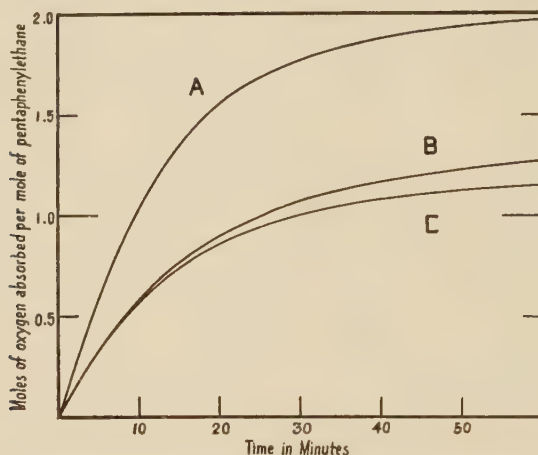


FIG. 1.—Rate of oxygen absorption by 0.025 molar solution of pentaphenylethane in *o*-dichlorobenzene at 94.40°. Curve A, in presence of 3 moles of pyrogallol; Curve B, oxygen pressure: 1 atmos.; Curve C, oxygen pressure: 0.2 atmos. (All experimental points fall on the curves.)

pressure of oxygen (1 atmos.) and therefore the concentration of dissolved oxygen remained constant throughout a run. A definite decision between the two mechanisms was obtained for pentaphenylethane by comparing the rates of reaction when pure oxygen and air (0.2 oxygen) were employed. The rate according to the first mechanism (bimolecular) should be decreased to one-fifth of its value by changing from oxygen to air, while the rate according to the second mechanism (unimolecular), involving radicals, should remain unchanged.

In Fig. 1, Curves B and C, are plotted the time rates of oxygen absorption by a 0.025 molar solution of pentaphenylethane in *o*-dichlor-

obenzene at 94.40° for oxygen pressures of 1 and 0.2 atmos., respectively. A comparison of the rates of oxygen absorption with different partial pressures by a solution of pentaphenylethane is complicated by side reactions, leading to the absorption of more than one mole of oxygen, for which the extent and perhaps the rate increases with the oxygen pressure. From an inspection of the curves, however, it is evident that initially the rate of absorption of oxygen is independent of the pressure; *i.e.*, the principal reaction is of the first order; the rate-controlling step is therefore a unimolecular process, and the direct reaction between oxygen and pentaphenylethane is eliminated from consideration.

For a unimolecular reaction the rate of absorption of oxygen throughout the reaction would be proportional to the concentration of pentaphenylethane:

$$dx/dt = k(a - x),$$

(k being the usual first-order velocity constant). The integrated equation, which is commonly used, is:

$$k = \frac{2.3}{t} \log \frac{a}{(a - x)}.$$

By considering the fraction, $Z = x/a$, of pentaphenylethane reacted the equation simplifies to:

$$k = \frac{-2.3}{t} \log (1 - Z).$$

If we assume any side reactions (which account for the absorption of more than one mole of oxygen) are negligible during the early course of the reaction we may calculate Z as the ratio of the actual absorption of oxygen in time, t , to the theoretical absorption assuming 100 per cent. unsymmetrical peroxide formation (see Fig. 2). The slopes of the lines, which, multiplied by 2.3, give the velocity constant, k , passing through the first four or five points differ by only 10 per cent., a difference which may be attributed entirely to the difference in total absorption of oxygen and not to any fundamental difference in the reaction rate. We have verified this independence of the rate on the oxygen pressure at temperatures from 85° to 100°. The values of the rate constants, as determined from the minimum slopes through the first reliable points, are recorded in Table IV. The most obvious mechanism for the oxidation of pentaphenylethane, then, is a relatively slow dissociation of the compound into two free radicals followed by a rapid reaction of oxygen with the radicals. The rate of oxidation is a measure of the rate of dissociation, there being no chain reactions under these conditions.

In the presence of pyrogallol in any ratio greater than two moles per mole of pentaphenylethane exactly two moles of oxygen per mole of pentaphenylethane was absorbed (Fig. 1, Curve A); the rate of absorption

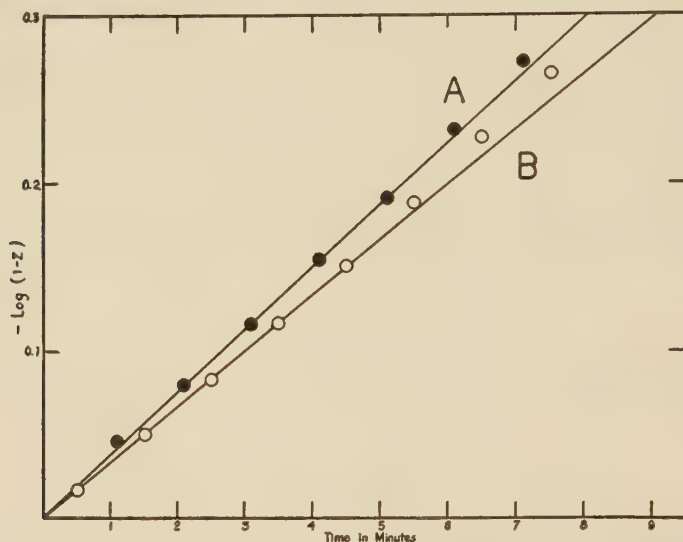


FIG. 2.—Rate of oxygen absorption by 0.025 molar solution of pentaphenylethane in *o*-dichlorobenzene at 94.40°. Curve A, filled circles, oxygen; Curve B, open circles, air. (Note that $-\log (1 - Z) = 0.3$ corresponds to 50 per cent. reaction). k from Curve A = 0.0855, from Curve B = 0.0756.

TABLE IV
VELOCITY CONSTANTS FOR ABSORPTION OF OXYGEN BY PENTAPHENYLETHANE IN *o*-DICHLOROBENZENE

p_{O_2}	CONC. (MOLES PER LITER)	84.70°	89.55°	94.40°	99.30°
1.0	0.1				0.148
1.0	0.05	0.0306			
1.0	0.025	0.0287		0.0855	
0.2	0.05	0.0309	0.0483	0.0889	0.134
0.2	0.025	0.0260	0.0490	0.0761	0.148
0.2	0.025	0.0276			
Average.....		0.0287	0.0486	0.0835	0.143

was correspondingly doubled. The reaction was strictly of the first order throughout 75–90 per cent. of the reaction (Fig. 3), and the rate was totally independent of the volume of solvent, the amount of pyrogallol (in excess of two moles), or the oxygen pressure. A temperature of 95° was adopted

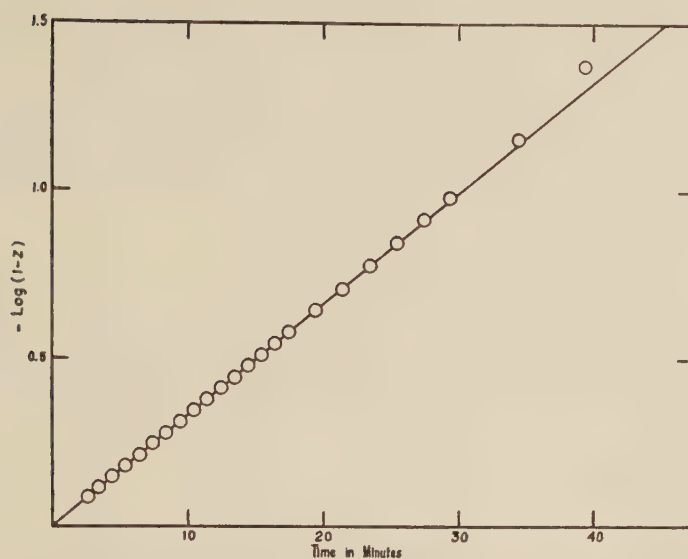


FIG. 3.—Rate of oxygen absorption by 0.025 molar solution of pentaphenylethane in *o*-dichlorobenzene at 94.40° in presence of 3 moles of pyrogallol; oxygen pressure = 0.2 atmos. A typical run. ($-\log (1 - Z) = 1.0$ corresponds to 90 per cent. reaction).

TABLE V
VELOCITY OF ABSORPTION OF OXYGEN BY PENTAPHENYLETHANE IN *o*-DICHLOROBENZENE AT 94.40° UNDER VARIOUS CONDITIONS

CONCENTRATION OF PENTAPHENYLETHANE (MOLES PER LITER)	MOLES PYROGALLOL PER MOLE PENTAPHENYLETHANE	p_{O_2}	k
0.025	1.0	0.2	0.0671*
0.025	2.0	0.2	0.0771
0.025	3.0	0.2	0.0795
0.025	3.0	0.2	0.0766
0.025	3.0	0.2	0.0754
0.025	3.9	1.0	0.0755
0.017	10.0	0.2	0.0762
0.05	1.4	0.2	0.0775
0.05	1.9	0.2	0.0745
0.05	2.0	1.0	0.0804
0.05	3.0	0.2	0.0770
Average of all reliable runs made.....			0.0765 ±0.004

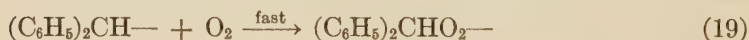
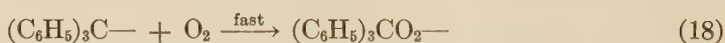
* Did not absorb the theoretical quantity of oxygen; insufficient pyrogallol to prevent formation of unsymmetrical peroxide.

as the most convenient for the study of the effect of varying the conditions. The results are collected in Table V. We have repeated the oxidations at five-degree intervals from 80° to 105°. The values of the rate constants and half-lives are given in Table VI. The agreement of the constants as determined in the presence and absence of pyrogallol is within 5 per cent. at 84.70° and 13 per cent. at 99.40°. Since the runs made in the presence of pyrogallol are capable of much greater precision we consider these values as the more reliable.

TABLE VI
VELOCITY OF OXYGEN ABSORPTION BY PENTAPHENYLETHANE IN PRESENCE OF
PYROGALLOL AT 80° TO 105°

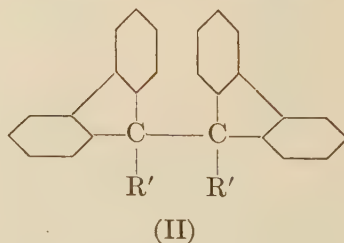
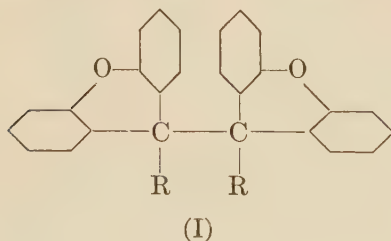
Temperature.....	79.85°	84.70°	89.55°	94.40°	99.30°	104.15°
Velocity constant (<i>k</i>).....	0.0163	0.0274	0.0462	0.0765	0.126	0.201
Half-life (min.).....	42.5	25.3	15.0	9.06	5.50	3.44
Number of runs.....	3	3	5	10	6	7
Mean error of mean (in per cent.).....	3.3	0.7	0.8	0.6	1.4	1.2

The mechanism of the oxidation of pentaphenylethane, therefore, is similar to that proposed for the oxidation of hexaphenylethane (Equations 17-19). The symmetrical and unsymmetrical peroxides may be formed



by combination of the appropriate radicals, but there is no direct reaction between a peroxide radical and pentaphenylethane. The pyrogallol stabilizes both peroxide radicals in the same manner as was observed for hexaphenylethane.

Conant and Evans concluded that they were measuring the rate of dissociation of a series of *s*-dialkyldixanthyls (Formula I) in their measurements of the rate of oxidation of these compounds.¹¹ Scherp, on the



¹¹ CONANT AND EVANS, *J. Am. Chem. Soc.* 51, 1925-1935 (1929).

other hand, has recently reported that a direct reaction between oxygen and diaryldifluoryls (Formula II) takes place.¹²

HEAT OF ACTIVATION OF THE DISSOCIATION PROCESS

The energy of activation for the dissociation of pentaphenylethane may be calculated from the velocity constants at different temperatures by the Arrhenius equation,

$$E_a = \frac{2.3RT_1T_2}{(T_2 - T_1)} \log \frac{k_2}{k_1}.$$

The values calculated from the experimental constants are: $E_{79.85-84.70^\circ} = 26.8$; $E_{84.70-89.55^\circ} = 27.8$; $E_{89.55-94.40^\circ} = 27.6$; $E_{94.40-99.30^\circ} = 27.7$; $E_{99.30-104.15^\circ} = 27.0$ kcal. The average was determined graphically, as is customary, from the equation written in the form,

$$\log k = \frac{E_a}{2.3R} (1/T) + C.$$

If $\log k$ is plotted against $(1/T)$ (Fig. 4), the slope of the line multiplied by 2.3 gives 27.6 kcal. as the heat of activation. We consider that this value is accurate to within ± 0.5 kcal.

The heat of activation of the dissociation of polyarylethanes is of considerable significance, since it represents a maximum value for the strength of the ethane linkage in the hydrocarbons. In Table VII are compared the half-lives and heats of activation of ethane and a number of substituted ethanes. It is seen that the half-life of pentaphenylethane in *o*-dichlorobenzene at 100° is approximately the same as the half-life of hexaphenylethane in toluene at 0° .

The heat of dissociation of pentaphenylethane could be calculated from measurements of the equilibrium constants at different temperatures, but we see no way of determining the position of equilibrium experimentally. The heat of dissociation is closely related to the heat of activation for the dissociation reaction, E_d , and the heat of activation for the reverse reaction, E_c , by the equation, $\Delta H = E_d - E_c$. It follows that the heat of dissociation cannot exceed the value 27.6 kcal. Of interest in this connection are some calculations made by Conant¹³ on the effects of different groups on the strength of the carbon-carbon bond. From a comparison of the heat of dissociation of dixanthyl and diphenyldixanthyl Conant has estimated the effect of replacing a hydrogen by a single phenyl group on the strength of the ethane linkage to be -11 kcal. The heat of dissociation

¹² SCHERP, *ibid.*, **58**, 576-580 (1936).

¹³ CONANT, *J. Chem. Phys.*, **1**, 427-431 (1933).

of pentaphenylethane would then be 11 kcal. greater than the heat of dissociation of hexaphenylethane¹⁴ (11.5 kcal.), or 22 kcal., a value which seems to us very reasonable.

We are now in a position to reinterpret several of the reactions of pentarylethanes as most likely taking place through radicals. Although cleavage by alkali metals is not a reaction of radicals, cleavage by bromine

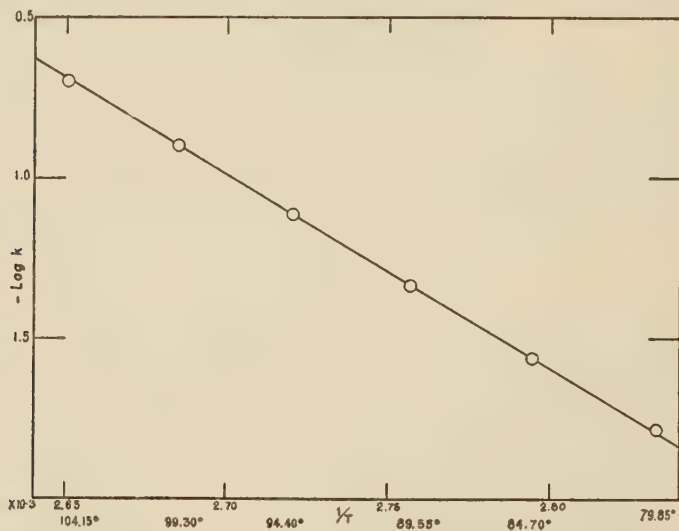


FIG. 4.—The rate of dissociation of pentaphenylethane at various temperatures

TABLE VII

HALF-LIFE AND HEAT OF ACTIVATION OF ETHANE AND SUBSTITUTED ETHANE DERIVATIVES

COMPOUND	HALF-LIFE (MIN.)	TEMP. (°C.)	SOLVENT	HEAT OF ACTIVATION (KCAL.)
Hexaphenylethane ⁹	4.7	0	Toluene	19.5
Pentaphenylethane.....	5.2	100	<i>o</i> -Dichlorobenzene	27.6
Dimethyldixanthyl ¹¹	55	35	Bromobenzene	34
Ethane.....				84

and hydrogen iodide,¹ by sulfuryl chloride¹⁵ and by phosphorus pentachloride¹⁶ probably involve only reaction of the reagents with the radicals. The products, tricyclohexyl- and dicyclohexylmethanes which Zartman and Adkins obtained by hydrogenation of pentaphenylethane at 125° are undoubtedly the result of hydrogenation of the intermediate radicals.¹⁷

¹⁴ ZIEGLER AND EWALD, *Ann.*, **473**, 180 (1929).

¹⁵ NORRIS, THOMAS AND BROWN, *Ber.*, **43**, 2945 (1910).

¹⁶ CONE AND ROBINSON, *ibid.*, **40**, 2166 (1907).

¹⁷ ZARTMAN AND ADKINS, *J. Am. Chem. Soc.*, **54**, 1668-1674 (1932).

EXPERIMENTAL

Because we had originally intended to use the Grignard reaction to prepare all the pentaarylethanes, we synthesized the triaryl- and diarylbromomethanes; the chlorides could undoubtedly be used with equal success for the sodium reactions. The preparation of triphenylbromomethane, the diarylbromomethanes, penta-phenylethane, 1,1,1,2-tetraphenyl-2-*p*-biphenylethane and 1,1,1-triphenyl-2,2-di-*p*-biphenylethane has been described previously.³

Diphenyl-p-biphenylbromomethane.—To prepare diphenyl-*p*-biphenylcarbinol 51.8 g. of phenyl *p*-biphenyl ketone was added to the Grignard reagent which had been prepared from 47.1 g. of bromobenzene in 90 cc. of anhydrous ether. After being refluxed for forty-five minutes, the clear solution was hydrolyzed with ice and dilute hydrochloric acid. The ether solution was concentrated and treated with petroleum ether (60–70°), whereupon 61.5 g. (92 per cent.) of the nearly pure carbinol, m. p. 132.5–134.5°, crystallized. A mixture of 33.6 g. of diphenyl-*p*-biphenylcarbinol, 15 cc. of benzene and 20 g. of acetyl bromide was heated on a steam bath for one hour. After addition of 100 cc. of petroleum ether (60–70°), 36.8 g. (92 per cent.) of the triarylmethyl bromide precipitated. Diphenyl-*p*-biphenylbromomethane crystallizes from benzene-petroleum ether in the form of colorless hexagonal plates; m. p. 127.5–128°.

Anal. Calc'd for $C_{26}H_{18}Br$: Br, 20.0. Found: Br, 20.0.

Phenyl-di-p-biphenylbromomethane.—The corresponding carbinol was prepared in 83 per cent. yield from di-*p*-biphenyl ketone and a slight excess of phenylmagnesium bromide in ether solution; it is entirely unnecessary to replace the ether by xylene as recommended by Schlenk¹⁸ in order to achieve addition. Forty-eight grams of phenyl-di-*p*-biphenylcarbinol was heated for two hours on a steam bath with 20 g. of acetyl bromide and 25 cc. of 30 per cent. hydrogen bromide in glacial acetic acid. After addition of 50 cc. of petroleum ether (60–70°) the mixture was cooled; the phenyl-di-*p*-biphenylbromomethane was filtered off (48.5 g.) and recrystallized from petroleum ether containing a small amount of benzene, from which it was obtained in small colorless crystals; yield, 77 per cent.; m. p. 145–146.5°. A low-melting form, m. p. 70–72°, which contained solvent of crystallization, was often obtained when a larger proportion of benzene was used for recrystallization.

Anal. Calc'd for $C_{31}H_{23}Br$: Br, 16.8. Found: Br, 17.0.

Tri-p-biphenylcarbinol.—Morton and Stevens¹⁹ have described a method for the preparation of this compound in small amounts from sodium, *p*-chlorobiphenyl and diethyl carbonate. By the simple expedient of adding the *p*-chlorobiphenyl and diethyl carbonate slowly to the sodium in hot benzene we found that the reaction began at once and all hazards involving the induction period were avoided so that much larger quantities could be run at one time. Thirty-three grams of sodium wire was suspended in 200 cc. of benzene in a two-liter round-bottomed flask provided with a return condenser, and the liquid was brought to gentle reflux. A solution of 120 g. of *p*-chlorobiphenyl and 23.6 g. (0.2 mole) of diethyl carbonate in 200 cc. of benzene was slowly added through the top of the condenser. A brown color on the sodium appeared immediately and the reaction was at no time violent. The mixture was heated for one hour after all the solution had been added; the excess sodium was then dissolved through addition of alcohol. Hydrolysis of the resulting mixture gave 60 g. of crude material which was contaminated, however, by considerable amounts of a very insoluble product. Recrystallization from benzene gave 42.5 g.

¹⁸ SCHLENK, *Ann.*, **363**, 298–300 (1909).

¹⁹ MORTON AND STEVENS, *J. Am. Chem. Soc.*, **53**, 4028 (1931).

(42 per cent.) of tri-*p*-biphenylcarbinol melting at 208–210°. Morton and Stevens reported a 23 per cent. yield of pure product in a smaller run.

Tri-p-biphenylbromomethane.—Fifteen grams of acetyl bromide was added to a suspension of 40 g. of tri-*p*-biphenylcarbinol in 50 cc. of benzene and the reaction mixture was heated for three hours on a steam bath. The bromide, which separated out on cooling, was recrystallized from benzene and dried in a vacuum desiccator over soda-lime and paraffin; yield, 43 g. (95 per cent.) of colorless needles melting at 207.5–208° to a brown liquid.

Anal. Calc'd for $C_{37}H_{27}Br$: Br, 14.5. Found: Br, 14.2.

Diphenyl-p-biphenylmethylmagnesium Bromide.—In a 500 cc. round-bottomed flask provided with a condenser and mercury trap were placed 19.95 g. of diphenyl-*p*-biphenylbromomethane, 1.232 g. of magnesium ribbon, 25 cc. of anhydrous ether and 50 cc. of dry benzene; the air was then removed and replaced by nitrogen. The solution, protected from light by a black cloth, was refluxed for ten hours. The characteristic red color of the free radical, diphenyl-*p*-biphenylmethyl, developed immediately and gradually gave way to the lighter brown color of the Grignard reagent. Since 0.100 g. of magnesium was recovered, the yield of Grignard reagent was calculated to be 85 per cent.

Phenyl-di-p-biphenylmethylmagnesium Bromide.—The Grignard reagent was prepared from 2.375 g. of pure phenyl-di-*p*-biphenylbromomethane and 0.285 g. of magnesium, activated by iodine, in 6 cc. of ether and 11 cc. of benzene. After one hour of refluxing in a nitrogen atmosphere the filtered solution was hydrolyzed with excess of standard acid which was titrated with standard alkali. The yield of Grignard reagent as determined from the loss in weight of the magnesium and from titration was quantitative. The successful preparation of the Grignard reagent is contingent on the purity of the bromide.

Attempts to Prepare Tri-p-biphenylmethylmagnesium Bromide.—In the attempts to prepare the Grignard reagent from 2.735 g. of tri-*p*-biphenylbromomethane and 0.24 g. of magnesium in 15 cc. of ether and 30 cc. of benzene iridescent green needles formed on the magnesium and sides of the flask immediately. Continued refluxing over a period of several hours gave a colorless precipitate which proved to be tri-*p*-biphenylmethane (yield 62 per cent.). No appreciable loss in the weight of the magnesium could be detected.

In order to prepare the double salt a solution of anhydrous magnesium bromide, prepared from 3.6 g. of mercuric bromide and excess of magnesium in 20 cc. of ether and 40 cc. of benzene, was filtered into a benzene solution of 1.1 g. of tri-*p*-biphenylbromomethane. The double salt, which precipitated immediately, was filtered off and washed by digestion with hot benzene. The crystals were immediately decomposed by a solution of potassium hydroxide in methanol. Quantitative estimation of bromine, magnesium and the organic product, the methyl ether of tri-*p*-biphenylcarbinol, (m. p. 162–163°), indicated the composition: $2(C_6H_5-C_6H_4)_3CBr \cdot 3MgBr_2$. In another experiment the double salt prepared from 2.75 g. of tri-*p*-biphenylbromomethane was refluxed in ether-benzene for a day; from the mixture 1.72 g. (73 per cent.) of tri-*p*-biphenylmethane was isolated.

Synthesis of Pentaarylethanes through the Sodium Reaction.—Unless otherwise stated the pentaarylethanes were prepared by this reaction. To 45 g. of molten sodium under xylene in a 250-cc. Erlenmeyer flask 55 g. of mercury was added slowly from a medicine dropper. After the flask had cooled to room temperature the amalgam was carefully pipetted into a clean flask and stored under benzene. The density of the amalgam is approximately 2 g. per cubic centimeter.

To 10 g. of 45 per cent. sodium amalgam in a 70 cc. glass-stoppered bottle (the glass-stoppered graduated cylinders are most suitable) containing 20 cc. of ether and 30 cc. of benzene was added 0.01 mole of the triarylbromomethane. The bottle was repeatedly evacuated and filled with nitrogen and then sealed with special stop-cock grease.²⁰ The bottle was shaken by hand, cooling when necessary, until the characteristic color of the radical had changed to the intense color of the triarylmethyl-sodium compound; the bottle was then mechanically shaken for several hours. The sodium amalgam was now frozen by immersing the bottle in an ice-salt mixture, and 0.01 mole of the diarylbromomethane was added. In every case the intense color of the triarylmethylsodium disappeared completely on shaking the mixture, showing that the reaction was at an end almost immediately. The solution, containing a suspension of sodium bromide, was decanted from the solid amalgam into a separatory funnel. The amalgam was washed with benzene containing a small amount of alcohol and the washings were added to the main solution. When all the particles of amalgam in the separatory funnel had reacted with the alcohol, the ether-benzene solution was washed with dilute hydrochloric acid, and with water, dried, filtered, and evaporated at room temperature. Crystallization of the residual oil was accomplished by stirring with acetone or alcohol; the crude product was filtered, dried, and recrystallized.

1-p-Biphenyl-1,1,2,2-tetraphenylethane (1).—To the Grignard reagent, prepared in 86 per cent. yield from 19.95 g. of diphenyl-*p*-biphenylbromomethane as already described, was added 12.35 g. of diphenylbromomethane. After being refluxed for two hours the reaction mixture was hydrolyzed with dilute acetic acid. The dark-red oil, which was obtained from the ether-benzene solution, crystallized when stirred with a mixture of acetone and methanol. Two recrystallizations from chloroform-alcohol yielded 16.8 g. (80 per cent., based on the Grignard reagent) of 1-*p*-biphenyl-1,1,2,2-tetraphenylethane in the form of colorless, refracting prisms, melting at 190–192° to a light red liquid.*

Anal.† Calc'd for $C_{26}H_{20}$: C, 93.8; H, 6.2.

Found: C, 93.6; H, 6.4.

1,2-Di-p-biphenyl-1,1,2-triphenylethane (1,2).—To the Grignard reagent from 13.3 g. of diphenyl-*p*-biphenylbromomethane was added 10.77 g. of phenyl-*p*-biphenylbromomethane. After standing at room temperature for twelve hours the mixture was hydrolyzed. The residue obtained by evaporation of the organic solvents crystallized when stirred with acetone. Recrystallization of the pentaarylethane from chloroform-alcohol gave 7.76 g. (46 per cent.) of diamond-shaped plates, melting at 180–185° to an orange-red liquid, the solid acquiring a color at about 170°. A 77 per cent. yield of the same compound of m.p. 172–178° was obtained through the sodium reaction; recrystallization raised the melting point to 180–185°.

Anal. Calc'd for $C_{34}H_{24}$: C, 93.9; H, 6.1.

Found: C, 93.6; H, 6.3.

²⁰ MELOCHE AND FREDERICK, *ibid.*, **54**, 3264 (1932).

* For determining the melting points of all the pentaarylethanes the melting-point tube containing the material was placed in a test-tube which was repeatedly evacuated and filled with nitrogen; just before inserting the tube in the bath, which was preheated to within 20–30° of the melting point, the open end was sealed.

† In order to drive off the solvent of crystallization it was necessary to fuse the pentaarylethane under reduced pressure; all the pentaarylethanes, except the 1,1,1,2- and the 1,1,1,2,2- were brought to incipient fusion.

1,2,2-Tri-p-biphenyl-1,1-diphenylethane (1,2,2-).—A 75 per cent. yield of crude pentaarylethane was obtained by coupling diphenyl-*p*-biphenylmethylsodium with di-*p*-biphenylbromomethane. Recrystallization from chloroform, acetone, carbon tetrachloride, ether, petroleum ether or from benzene invariably gave a product which melted between 100° and 150° with effervescence, indicating the presence of solvent of crystallization. A sample which had been allowed to stand for several months melted at 227–230°, with previous softening at 223°.

Anal. Calc'd for $C_{50}H_{38}$: C, 94.0; H, 6.0.

Found: C, 93.7; H, 6.2.

1,1-Di-p-biphenyl-1,2,2-triphenylethane (1,1-).—The yield of crude pentaarylethane prepared from phenyl-di-*p*-biphenylmethylsodium and diphenylbromomethane was 89 per cent. The hydrocarbon crystallizes from chloroform-alcohol as colorless, diamond shaped plates, melting at 198–199° to a dark-red liquid, with decomposition beginning at 193°. Interaction of the Grignard reagent from phenyl-di-*p*-biphenylbromomethane and diphenylbromomethane gave a deeply colored oil from which no pentaarylethane crystallized.

Anal. Calc'd for $C_{44}H_{34}$: C, 93.9; H, 6.1.

Found: C, 93.9; H, 6.3.

1,1,2-Tri-p-biphenyl-1,2-diphenylethane (1,1,2-).—The crude pentaarylethane was isolated in 72 per cent. yield. By recrystallization from chloroform-alcohol the hydrocarbon was obtained in the form of colorless prisms (64 per cent. yield), melting at 206–209° to an intensely dark-brown liquid, the solid turning orange at 190°.

Anal. Calc'd for $C_{50}H_{38}$: C, 94.0; H, 6.0.

Found: C, 94.2; H, 6.2.

1,1,2,2-Tetra-p-biphenyl-1-phenylethane (1,1,2,2-).—A 66 per cent. yield of product melting above 214° was obtained. By recrystallization from chloroform-alcohol the 1,1,1,2- compound was obtained in clusters of blunt, colorless needles; m. p. 222–228°, the solid darkening at 210°.

Anal. Calc'd for $C_{56}H_{42}$: C, 94.1; H, 5.9.

Found: C, 93.9; H, 6.1.

1,1,1-Tri-p-biphenyl-2,2-diphenylethane (1,1,1-).—This compound was obtained in 79 per cent. yield; recrystallization from chloroform-alcohol gave four-sided prisms, melting at 164–167° to a greenish-yellow fluorescent liquid; the melt turns red on heating to a higher temperature.

Anal. Calc'd for $C_{50}H_{38}$: C, 94.0; H, 6.0.

Found: C, 93.9; H, 6.3.

1,1,1,2-Tetra-p-biphenyl-2-phenylethane (1,1,1,2-).—A 51 per cent. yield of colorless needles was obtained when the crude product was recrystallized from chloroform-alcohol. If heated very slowly from room temperature the product melted at 215–220° to a dark-red liquid, the solid turning dark at 195°. If inserted in the melting point bath above 177°, however, the solid instantly melted and almost instantly resolidified to melt again at 223–226°.

Anal. Calc'd for $C_{56}H_{42}$: C, 94.1; H, 5.9.

Found: C, 93.7; H, 6.0.

1,1,1,2,2-Penta-p-biphenylethane (1,1,1,2,2-).—This pentaarylethane was obtained in two forms. The low-melting form crystallized in fine interlocking needles from a chloroform-alcohol solution, melting at 172–185° to a red liquid. If the pentaarylethane was allowed to stand in contact with the solvent or was recrystallized from benzene colorless rhombic plates of the high-melting form were obtained;

melting point 226–234° (black opaque liquid), the solid turning dark and sintering at 210°. The yield of pure material was 63 per cent.

Anal. Calc'd for $C_{62}H_{46}$: C, 94.1; H, 5.9.

Found: C, 94.5; H, 5.9.

Cleavage by Hydrogen Iodide.—A mixture of 0.2 g. of iodine and 0.6 g. of red phosphorus was allowed to react in 20 cc. of acetic acid until the iodine color disappeared; 0.3 cc. of water and 0.0025 mole of pentaarylethane were added and the mixture was refluxed in a nitrogen atmosphere for one hour.¹ In no case was any unreacted pentaarylethane recovered. The separation of the triarylmethane and diarylmethane depended upon the relative solubilities of the cleavage products. In the cleavage of the 1-, 1,1- and 1,1,1-, all of which gave diphenylmethane, the reaction mixture following removal of the solvent was extracted with 30–40° petroleum ether leaving the triarylmethane as a residue. Recrystallization gave yields of triarylmethane of 90 per cent., 98 per cent. and 94 per cent. respectively; in each case a 61 per cent. yield of diphenylmethane was isolated.

Since tri-*p*-biphenylmethane is insoluble in cold chloroform, in which the diarylmethanes are soluble, the products from the cleavage of the 1,1,1,2- and 1,1,1,2,2- were extracted with chloroform. The yields of tri-*p*-biphenylmethane were 90 per cent. and 82 per cent.; those of the diarylmethanes were 78 per cent. and 99 per cent. respectively.

In the cleavage of the 1,1,2- compound the products were separated by dissolving the phenyl-*p*-biphenylmethane in 60–70° petroleum ether; the yields of triarylmethane and diarylmethane were 76 per cent. and 69 per cent. respectively.

Phenyl-di-*p*-biphenylmethane and di-*p*-biphenylmethane, obtained from the cleavage of the 1,1,2,2- were isolated by cooling a benzene solution of the mixture, whereupon the latter compound crystallized. By removing the benzene and taking up the oil in acetone and cooling, the phenyl-di-*p*-biphenylmethane was deposited; yields of 26 per cent. and 30 per cent. respectively were isolated.

Cleavage products from the 1,2- and 1,2,2- were identified by allowing the solutions to evaporate slowly to dryness and mechanically separating the different crystals.

Cleavage by Sodium Amalgam.—The procedure was the same as that previously described¹ except that more solvent was used. A solution of 0.0015 mole of the pentaarylethane in 20 cc. of ether and 10 cc. of benzene in a 70-cc. glass-stoppered bottle was shaken for twenty-four hours with (a) 30 g. of 1 per cent. sodium amalgam, and (b) 7 g. of 45 per cent. sodium amalgam. The extent of the reaction was determined by freezing out the sodium amalgam and titrating the colored organometallic compounds with a 0.6 normal solution of alcohol in benzene, the end point being the complete disappearance of the color. For the titration the glass stopper of the reaction bottle was quickly replaced by a rubber stopper containing the burette tip. The flask was evacuated through the burette, which was then filled with the standard solution. As soon as the bottle had been chilled a small cork was inserted in the top of the burette and the alcohol solution was quickly added, with shaking, until the color disappeared. A correction was applied for the volume of solution used to fill the tip of the burette. The accuracy of the method, although limited by the trapping of some of the colored sodium compounds by the solid amalgam and also by the reaction of the sodium in the amalgam with alcohol, is considerably greater than any results based upon the separation and isolation of the reaction products from the unreacted pentaarylethane.

The only pentaarylethane to give a color with 1 per cent. sodium amalgam in twenty-four hours was the 1,2,2- which gave a very faint purple color; titration indicated less than 0.1 per cent. cleavage and the original pentaarylethane was recovered. With 45 per cent. sodium amalgam the highly colored triarylmethyl- and diarylmethylsodium compounds formed fairly rapidly. The titrations of all the pentaarylethanes containing two or more biphenyl groups, with one exception, indicated between 94 per cent. and 105 per cent. cleavage; the 1,1,1- was apparently only 2 per cent. cleaved and we attribute this result to the probable presence of chloroform of crystallization which reacted with the cleavage products. Titration of the cleavage products from the 1,1- was inadvertently spoiled but an 88 per cent. yield of the triarylmethane was isolated. In two experiments the cleavage of the 1- was 49 per cent. and 38 per cent.; the 2- was cleaved to the extent of 32 per cent. and 64 per cent. The differences between the two values are attributed chiefly to the physical condition of the amalgam during the reaction. The amalgam when shaken exhibits a tendency to disperse into a finely divided form; whenever this happened there was an induction period of two to four hours before the appearance of any color, which otherwise became noticeable within a relatively few minutes.

When a solution of 0.615 g. of pentaphenylethane in 20 cc. each of ether and benzene was shaken with 45 per cent. sodium amalgam for thirty days the color was brown rather than red, as it should have been for cleavage to $(\text{C}_6\text{H}_5)_3\text{CNa}$, and hydrolysis gave no triphenylmethane, the original pentaarylethane being recovered in 85 per cent. yield. It is quite probable that the sodium displaced the hydrogen to give pentaphenylethylsodium, $(\text{C}_6\text{H}_5)_3\text{C}-\text{CNa}(\text{C}_6\text{H}_5)_2$, a reaction similar to that reported by Dorfman, who found that pentaphenylethylpotassium is formed by the interaction of pentaphenylethane and phenylisopropylpotassium.²¹

Thermal Decomposition.—(213°) A solution of 0.972 g. of 1-*p*-biphenyl-1,1,2,2-tetraphenylethane in 10 cc. of ethyl benzoate was refluxed for one hour in a nitrogen atmosphere. The characteristic orange-red color of the diphenyl-*p*-biphenylmethyl radical soon gave way to a darker brown. The solvent was removed by distillation under reduced pressure at 100°; the dark-red oil was taken up in benzene and decolorized with norit; on cooling 0.155 g. (46 per cent.) of *s*-tetraphenylethane crystallized.

A solution of 1.580 g. of penta-*p*-biphenylethane in 20 cc. of ethyl benzoate was refluxed for one hour in a nitrogen atmosphere; the residue, after removal of the solvent at 100°, in chloroform gave 0.335 g. (52 per cent.) of *s*-tetra-*p*-biphenylethane.

(100–110°) A solution of 1.025 g. of pentaphenylethane in 15 cc. of toluene was refluxed in a nitrogen atmosphere for seventeen hours. The toluene was allowed to evaporate at room temperature; the light-yellow oil partially crystallized when stirred with benzene and petroleum ether; 0.125 g. (30 per cent.) of pure *s*-tetraphenylethane was isolated. From the filtrate 0.030 g. of pentaphenylethane was recovered. In a similar experiment with 2.05 g. of pentaphenylethane in 25 cc. of toluene after eight hours of refluxing the pentaphenylethane was recovered in 20 per cent. yield; a 10 per cent. yield of *s*-tetraphenylethane was isolated.

A solution of 0.790 g. of penta-*p*-biphenylethane in 11 cc. of *o*-dichlorobenzene was heated at 100° for two hours in a nitrogen atmosphere. A total of 0.685 g. (87 per cent.) of penta-*p*-biphenylethane was recovered; fractional crystallization established the absence of any *s*-tetra-*p*-biphenylethane in the recovered product; from the filtrate 0.005 g. of *s*-tetra-*p*-biphenylethane was isolated.

Formation of Pentaphenylethane from Radicals.—To a mixture of 0.01 mole each of

²¹ DORFMANN, *ibid.*, 57, 1457 (1935).

triphenylchloromethane and diphenylbromomethane in a 70-cc. glass-stoppered bottle containing 40 cc. of benzene was added 2 cc. of mercury. The air was displaced by nitrogen and the bottle was shaken for one day. The nearly colorless solution was filtered from the mercury and mercurous salts, and the solvent was allowed to evaporate at room temperature. The oil was crystallized by stirring with alcohol and again allowed to evaporate in order to crystallize any triphenylmethyl peroxide which might have been formed. Since the crystalline product was completely soluble in 10 cc. of warm chloroform, the presence of more than traces of the peroxide was excluded; by addition of alcohol a 95 per cent. yield of pentaphenylethane melting at 176–180° was isolated. In another experiment the triphenylchloromethane was first shaken with the mercury for eight hours in order to convert it to triphenylmethyl. Then the diphenylbromomethane was added and the mixture was shaken for thirty-six hours. At the end of the time no radical remained; on working up the mixture an 88 per cent. yield of pure pentaphenylethane (melting point 182–183°) was isolated.

Oxygen Absorption by Pentaarylethanes at 100°.—The apparatus consisted of a 200-cc. round-bottomed flask provided with an interchangeable ground-glass stopper carrying an entrance tube which was connected to a 100-cc. gas burette by heavy rubber tubing. A three-way stopcock in the line provided for evacuating and filling the system with oxygen. The burette was provided with a water jacket and leveling tube by which the system could be maintained at atmospheric pressure throughout the run. The procedure for a typical run was as follows: 25 cc. of redistilled *o*-dichlorobenzene was placed in the absorption flask which was connected to the gas burette, filled with oxygen, and mechanically shaken while completely immersed in a steam cone for twenty minutes; during this period the level of the *o*-dichlorobenzene used as retaining liquid in the gas burette was brought to the 100 cc. mark. The flask was then cooled to room temperature, finally being placed in a large beaker of water until the burette reading (about 45 cc.) became constant; the difference in readings represented the expansion of gas due to the rise in temperature. The flask was now opened; 0.00125 mole of pentaarylethane was introduced and the system was refilled with oxygen. After shaking by hand for a few minutes to saturate the solvent the flask was again placed in the beaker of water and the burette reading was adjusted to the same value as before. Since the increase in volume due to the expansion had just been measured under identical conditions, the initial reading when the flask containing the pentaarylethane solution was at 100° was now known (100 cc.). The flask was now placed in the steam bath and connected to a mechanical shaker operated by a water motor; the steam was turned on, and readings were taken periodically until the rate of absorption became constant, when the flask was removed from the steam bath and cooled as before described. The total absorption was determined from the difference in volume at room temperature and from the difference in volume of the system containing the solvent at 100°; as evidence for the reliability of the method the two usually gave results agreeing to within 0.3 cc. The moles of oxygen absorbed per mole of pentaarylethane were calculated from the measured absorption, the burette temperature and the atmospheric pressure.

Triphenylmethyl-(diphenylmethyl)-peroxide (C_6H_5)₃C—O—O—CH(C_6H_5)₂.—A solution of 0.1230 g. (0.03 mole) of pentaphenylethane in 25 cc. of *o*-dichlorobenzene was shaken at 100° in an oxygen atmosphere for twenty minutes. In this time 110 per cent. of the theoretical amount of oxygen was absorbed and the solution acquired a yellow color. The solvent was removed by distillation under reduced pressure at 100°, and the residual oil was taken up in acetone; from the solution 0.060 g. (12 per

cent.) of bis-triphenylmethyl peroxide was filtered off. The acetone was allowed to evaporate and the residue was taken up in alcohol; on standing the solution deposited 0.630 g. (48 per cent.) of the unsymmetrical peroxide. Triphenylmethyl-(diphenylmethyl)-peroxide crystallizes from petroleum ether in the form of colorless prisms; melting point 93–94° without decomposition. This unsymmetrical peroxide, in contrast to bis-triphenylmethyl peroxide, is very soluble in the usual organic solvents; it gives a yellow color with concentrated sulfuric acid. By carrying out the oxidation with air instead of oxygen a 69 per cent. yield of peroxide was isolated.

Anal. Calc'd for $C_{32}H_{26}O_2$: C, 86.8; H, 5.9.

Found: C, 86.7; H, 6.2.

Cleavage of Peroxide.—A mixture of 0.2210 g. of the aforementioned peroxide, 10 g. of 2 per cent. sodium amalgam, 20 cc. of ether, 30 cc. of benzene and a few drops of absolute alcohol was shaken for twenty-four hours. The reaction mixture was hydrolyzed and the benzene-ether solution was dried, filtered and concentrated. By crystallization of the mixture from carbon tetrachloride a 72 per cent. yield of triphenylcarbinol was obtained; the filtrate gave a 54 per cent. yield of benzohydrol. In a parallel experiment 0.518 g. of bis-triphenylmethylperoxide was shaken with 5 g. of 2 per cent. sodium amalgam in 20 cc. of ether and 30 cc. of benzene. Even after five days 74 per cent. of the peroxide was recovered unchanged; only 19 per cent. of triphenylcarbinol was isolated. It was found that 45 per cent. sodium amalgam cleaves the symmetrical peroxide readily.* When 1.03 g. of triphenylmethyl peroxide was shaken with 45 per cent. sodium amalgam for twenty-four hours and the product was hydrolyzed, 0.975 g. (94 per cent.) of triphenylcarbinol was obtained.

Reaction with Methylmagnesium Iodide.—No gas was evolved when 5 cc. of 0.75 normal methylmagnesium iodide in *n*-butyl ether was added to 0.4262 g. of the unsymmetrical peroxide. Upon heating for forty-five minutes at 100° 88 per cent. of the calculated amount of gas was evolved, assuming the reaction:

$(C_6H_5)_3C-O-O-CH(C_6H_5)_2 + 2CH_3MgI \rightarrow (C_6H_5)_3COMgI + (C_6H_5)_2CHOMgI + C_2H_6$. The solution, after hydrolysis and removal of the *n*-butyl ether gave 64 per cent. of the theoretical amount of triphenylcarbinol and 59 per cent. of benzohydrol. Bis-triphenylmethylperoxide is not cleaved by the Grignard reagent under these conditions.

*Triphenylmethyl-(phenyl-*p*-biphenylmethyl)-peroxide* $(C_6H_5)_3C-O-O-CH(C_6H_5)-(C_6H_4-C_6H_5-p)$.—In twenty minutes at 100° 0.972 g. of the pentaarylethane in 25 cc. of *o*-dichlorobenzene absorbed 130 per cent. of the calculated amount of oxygen. The solvent was removed and the oil was taken up in acetone. Bis-triphenylmethyl peroxide in 9 per cent. yield (0.045 g.) crystallized out. The acetone was removed from the filtrate, and the residue was recrystallized from chloroform-alcohol, from which 0.600 g. (58 per cent.) of the unsymmetrical peroxide was obtained as colorless, rectangular prisms; melting point 129.5–130°. The peroxide gives a brownish-yellow color with concentrated sulfuric acid.

Anal. Calc'd for $C_{38}H_{30}O_2$: C, 88.0; H, 5.8.

Found: C, 88.0; H, 6.0.

Cleavage of Peroxide.—By shaking 0.2590 g. of the aforementioned unsymmetrical peroxide with 2 per cent. sodium amalgam for two days an 84 per cent. yield of triphenylcarbinol and a 41 per cent. yield of 4-phenylbenzohydrol were obtained. The two products were separated by recrystallization from carbon tetrachloride, from which the triphenylcarbinol separated; the *p*-phenylbenzohydrol in the filtrate was recrystallized from benzene and petroleum ether.

* ZIEGLER AND THIELMANN, *Ber.*, **56B**, 1742 (1923), observed the cleavage of bis-triphenylmethyl peroxide by potassium, giving triphenylcarbinol.

Triphenylmethyl-(di-p-biphenylmethyl)-peroxide $(C_6H_5)_3C-O-O-CH(C_6H_4-C_6H_5-p)_2$.—For the preparation of this peroxide fifteen minutes was allowed for the oxidation of 1.404 g. of the pentaarylethane; 116 per cent. of the theoretical amount of oxygen was absorbed. After removal of the solvent and digestion of the product with acetone 0.130 g. of an insoluble material, probably a mixture of the symmetrical peroxide and di-*p*-biphenyl ketone, and 0.815 g. (55 per cent.) of the unsymmetrical peroxide were isolated. Recrystallization from chloroform-alcohol gave colorless crystals of triphenylmethyl-(di-*p*-biphenylmethyl)-peroxide; melting point 148–149°.

Anal. Calc'd for $C_{44}H_{34}O_2$: C, 88.8; H, 5.8.

Found: C, 88.3; H, 6.0.

Cleavage of Peroxide.—A mixture of 0.1919 g. of the aforementioned peroxide, 10 g. of 2 per cent. sodium amalgam, 0.5 cc. of absolute alcohol, 20 cc. of ether and 30 cc. of benzene was shaken for seven days. The reaction mixture was hydrolyzed, the ether-benzene solution was filtered, dried and concentrated. Since the mixture of carbinols could not be separated the solvent was removed and the oil was treated with a solution of 0.09 g. of chromic anhydride in 9 cc. of acetic acid. After standing at room temperature for fifty minutes the mixture was poured into water; the precipitate was extracted with benzene and the solution was concentrated. From the solution 0.0828 g. (76 per cent.) of di-*p*-biphenyl ketone precipitated; from the filtrate 0.0456 g. (54 per cent.) of triphenylcarbinol was isolated.

The peroxide was also cleaved by sulfuric acid. A solution of 0.594 g. in 10 cc. of concentrated sulfuric acid gave a dark-green color which soon changed to orange. The solution was poured into water and extracted with chloroform, using in all 300 cc. The chloroform was removed and the residue dissolved in hot carbon tetrachloride; on cooling 0.225 g. (86 per cent.) of triphenylcarbinol crystallized.

Thermal Decomposition of Peroxide.—The triphenylmethyl-(di-*p*-biphenylmethyl) peroxide (0.3253 g.) was heated in an oil bath at 180° in a nitrogen atmosphere for one hour; from the resulting oil there was isolated 0.0759 g. (41 per cent.) of di-*p*-biphenyl ketone and a trace (0.004 g.) of triphenylcarbinol.

Diphenyl-p-biphenylmethyl-(di-p-biphenylmethyl)-peroxide $(p-C_6H_5-C_6H_4)-(C_6H_5)_2C-O-O-CH(C_6H_4-C_6H_5-p)_2$.—From the reaction products obtained by one-hour oxidation of 0.797 g. of the (1,2,2-) ethane there was isolated a trace of di-*p*-biphenyl ketone and 0.400 g. (48 per cent.) of the unsymmetrical peroxide. This peroxide crystallizes from benzene and petroleum ether in colorless prisms; it melts at 161° with decomposition, the melt solidifies and remelts again by 194–197°; the result is probably due to the di-*p*-biphenyl ketone (melting point 236°) formed in the pyrolysis.

Anal. Calc'd for $C_{50}H_{38}O_2$: C, 89.5; H, 5.7.

Found: C, 89.8; H, 5.9.

Phenyl-di-p-biphenylmethyl-(diphenylmethyl)-peroxide $(C_6H_5)(p-C_6H_5-C_6H_4)_2-C-O-O-CH(C_6H_5)_2$.—This peroxide was obtained when 1.124 g. (0.002 mole) of the pentaarylethane (1,1-) was heated on a steam bath for thirty minutes, 103 per cent. of the calculated amount of oxygen having been absorbed in this time. From acetone-alcohol 0.77 g. (65 per cent.) of the peroxide crystallized in the form of colorless tetragonal prisms; the pure product melts at 151–152° and gives a wine-red color with sulfuric acid.

Anal. Calc'd for $C_{44}H_{34}O_2$: C, 88.8; H, 5.8.

Found: C, 88.8; H, 6.1.

Cleavage of Peroxide.—For the cleavage 0.2970 g. of the peroxide was shaken with 10 g. of 2 per cent. sodium amalgam, 0.5 cc. of absolute alcohol, 25 cc. each of ether and benzene for five days. The colorless solution was hydrolyzed, filtered and concentrated. The secondary alcohol was dissolved in petroleum ether, leaving

the tertiary alcohol as an insoluble residue. Phenyl-di-*p*-biphenylcarbinol was isolated in 89 per cent yield, benzohydrol in 55 per cent yield.

Tri-p-biphenylmethyl-(phenyl-p-biphenylmethyl)-peroxide $(p-C_6H_5-C_6H_4)_3-C-O-O-CH(C_6H_5)(C_6H_4-C_6H_5-p)$.—When 1.071 g. of the (1,1,1,2-) pentaarylethane was shaken with oxygen for ten minutes the absorption was 103 per cent.; 0.960 g. (86 per cent.) of the unsymmetrical peroxide was isolated. Recrystallization from chloroform-alcohol gave 0.900 g. (80 per cent.) of colorless needles; melting point 168°. The peroxide gave a purple-red color with concentrated sulfuric acid.

Anal. Calc'd for $C_{56}H_{42}O_2$: C, 90.0; H, 5.7.

Found: C, 90.0; H, 5.9.

Cleavage of Peroxide.—A solution of 0.3730 g. of the peroxide was shaken for fourteen days with 10 g. of 2 per cent. sodium amalgam in 25 cc. each of ether and benzene and 0.5 cc. of alcohol. From a benzene solution 0.1788 g. (73 per cent.) of tri-*p*-biphenylcarbinol was isolated; the filtrate in petroleum ether (60–70°) gave 0.402 g. (31 per cent.) of 4-phenylbenzohydrol.

Oxygen Absorption by Pentaphenylethane at 80° to 105°.—The oxygen absorptions were carried out in a large air thermostat the temperature of which could be maintained constant to within $\pm 0.05^\circ$. To obtain consistent rate measurements it was found necessary to allow the thermostat to attain thermal equilibrium before making any runs; at the higher temperatures this required from three to four hours. The absorption vessel and gas burette were the same as previously described for the oxidation of pentaarylethanes at 100°. The flask was held in a metal cup by spring clamps and was shaken at a speed of 700 r. p. m. A short 40–110° thermometer, graduated in fifths of a degree and calibrated against a Bureau of Standards thermometer, was mounted in the box with the bulb about 2 cm. from the absorption flask. The pentaphenylethane was purified by dissolving it in hot benzene (2 cc. per g.) and precipitating it by adding warm alcohol (5 cc. per g.) followed by cooling. The filtered product was dried at room temperature and then for six hours at 100° under reduced pressure. When the pentaphenylethane was recrystallized from chloroform-alcohol, ether or petroleum ether it was impossible to remove the solvent without decomposing the product. *o*-Dichlorobenzene was used as the solvent and as a retaining liquid in the burette; the vapor pressure was neglected in the calculations.

Preliminary experiments showed that neither solid pentaphenylethane nor a pyrogallol solution alone absorbs any oxygen at 100°. The procedure for a typical run was as follows, 50 cc. of redistilled *o*-dichlorobenzene was saturated with oxygen (or air) by shaking in the absorption flask at the desired temperature for from ten to fifteen minutes at 100°; then approximately 0.00125 mole of pentaphenylethane, which had been weighed to 0.1 mg. in a small thin-walled glass bulb, was carefully introduced along with several glass chips in the flask and reinserted in the thermostat. After the temperature had again been brought to 100° the flask was gently rocked by rotating the shaker shaft, which extended through the box, and then the system was allowed to stand until the burette reading became constant. In this manner the entire system was at the thermostat temperature and the solvent was saturated with oxygen from the start of the run. When the shaker was started the bulb broke and absorption of oxygen began. The pentaphenylethane dissolved rapidly and the time of solution probably affected only the first few readings. Burette readings were taken at periodic intervals such that there would be from six to ten during the first half of the reaction period. In all runs the burette was filled with oxygen; in this way the partial pressure of oxygen in the absorption flask when air was used remained constant at 0.2 atmos. The only variation for the pyrogallol experiments was the addition of the vacuum-distilled pyrogallol to the solvent at the beginning

of the run. The solution of the pyrogallol often required fifteen to thirty minutes. The theoretical oxygen absorption was calculated from the equation,

$$V = (2) 152.0 \frac{w(t + 273)}{b}$$

where w is the weight of pentaphenylethane, t the average temperature of the burette during the run and b is the barometric reading in mm. The factor 2 is used only in those runs with pyrogallol. The factor 152.0 is the value of $760R/M$, where R is the

TABLE VIII

TYPICAL DATA OBTAINED IN REPRESENTATIVE EXPERIMENT

Wt. pentaphenylethane, 0.5096 g.; 0.470 g. pyrogallol (3/1); 50 cc. *o*-dichlorobenzene; oxygen pressure, 0.2 atmos.; temp. 99.30°; burette temp., 31.1°; barometer, 735 mm.; theoretical absorption, 64.1 cc.; time correction, for start of run, 0.0 min.

TIME MIN.	BURETTE READING	ABSORPTION (CC.)	YET TO BE ABSORBED	$-\log$ (1 - Z)	Z FOUND	Z* CALC'D	DIFF.
0.00	98.4	0.00	64.1	0.0000	0.0000	0.0000	0.000
0.50	93.6	4.8	59.3	0.0338	0.075	0.061	+0.014
1.00	90.3	8.1	56.0	0.0587	0.126	0.119	+0.007
1.50	87.1	11.3	52.8	0.0843	0.176	0.173	+0.003
2.00	84.0	14.4	49.7	0.1105	0.225	0.223	+0.002
2.50	81.1	17.3	46.8	0.1367	0.270	0.271	-0.001
3.00	78.4	20.0	44.1	0.1625	0.312	0.316	-0.004
3.50	75.7	22.7	41.4	0.1899	0.354	0.357	-0.003
4.00	73.2	25.2	38.9	0.2170	0.393	0.397	-0.004
4.50	70.8	27.6	36.5	0.2446	0.431	0.434	-0.003
5.00	68.6	29.8	34.3	0.2716	0.465	0.468	-0.003
6.00	64.5	33.9	30.2	0.3269	0.529	0.531	-0.002
7.00	60.9	37.5	26.6	0.3820	0.585	0.587	-0.002
8.00	57.7	40.7	23.4	0.4377	0.635	0.636	-0.001
9.00	55.0	43.4	20.7	0.4909	0.677	0.679	-0.002
10.00	52.6	45.8	18.3	0.5444	0.714	0.717	-0.003
12.00	48.6	49.8	14.3	0.6516	0.777	0.780	-0.003
14.00	45.6	52.8	11.3	0.7538	0.824	0.830	-0.006
16.00	43.3	55.1	9.0	0.8527	0.860	0.868	-0.008
18.00	41.5	56.9	7.2	0.9496	0.888	0.897	-0.009
20.00	40.1	58.3	5.8	1.0435	0.910	0.920	-0.010

* Z calc'd is from the average rate constant at 99.30°, 0.126; the slope in the above run gave a value of 0.125 for the rate constant.

gas constant, 82.07, and M is the molecular weight of pentaphenylethane, 410.4. By subtracting the oxygen absorption from the theoretical absorption the volume yet to be absorbed was obtained; the logarithm of this volume was then subtracted from the logarithm of the theoretical oxygen absorption giving directly $-\log(1 - Z)$. Zero time was determined by extrapolation of the log.-time curve to $-\log(1 - Z) = 0.0$. The results and calculations of a typical run are recorded in Table VIII.

In the presence of pyrogallol the solution first turned pink and then became a dark brown; at the end of the oxidation considerable amounts of a dark-brown water-

soluble precipitate was present. From the combined products of several runs we were able to isolate benzophenone, as the oxime, but we found no triphenylcarbinol. Experiment showed that $(C_6H_5)_3COOH$, the primary oxidation product, undergoes extensive decomposition under the same conditions, yielding a dark-brown precipitate. That the unsymmetrical peroxide is not an intermediate product of the oxidation of pentaphenylethane in the presence of pyrogallol was proved by adding pyrogallol to a solution of pentaphenylethane that had already been oxidized in an oxygen atmosphere at 100° ; no absorption of oxygen took place.

SUMMARY

(1) A complete homologous series of pentaarylethanes containing phenyl and *p*-biphenyl groups has been synthesized. These compounds, although possessing a weakened carbon-carbon bond, do not dissociate at an appreciable rate at room temperature.

(2) The successive introduction of biphenyl groups progressively weakens the carbon-carbon bond.

(3) Solutions of pentaarylethanes rapidly absorb oxygen at 80 – 105° ; the principal products are the unsymmetrical peroxides, $R_3C-O-O-CHR_2$, although the oxidation proceeds only through the intermediate formation of triarylmethyl and diarylmethyl radicals.

(4) Pentaarylethanes in solution undergo *reversible* dissociation into free radicals in which the position of equilibrium is practically entirely in favor of the undissociated pentaarylethane.

(5) The rate of dissociation of pentaphenylethane is approximately the same at 100° as that of hexaphenylethane at 0° .

(6) The heat of activation for the dissociation of pentaphenylethane is 27.6 kcal., a value 50 per cent. greater than the corresponding value for hexaphenylethane.

